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Effect of pH on characterization and coagulation performance of poly-silicic-cation coagulant

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HIGHLIGHTS

- Poly-silicic-cation coagulants were prepared by synchronous-polymerization.
- New compounds are formed in PSiC and the crystal is influenced by pH.
- The optimal preparation pH for the structure and morphology of PSiC is 1.5.
- PSiC with pH of 1.5 exhibits the best coagulation performance.

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ABSTRACT

Poly-silicic-cation coagulants (PSiCs) with different pH were prepared by synchronous-polymerization. The characteristics and coagulation performances of the coagulants were analyzed. The results show that the crystal, structure and morphology of PSiC are influenced by pH and the optimal preparation pH is 1.5. The crystal analysis shows that some new complex compounds are formed in PSiC. The polymerization form and complexation degree of PSiC with pH of 1.5 are better than at other pH values. The structure and morphology analyses imply that the contents of ionic polymerized bonds, high polymers and irregular PSiC units decrease, and cross-copolymerization of Fe (III) and Al (III) hydroxyl polymers is weakened when pH is too low or too high. Coagulation experiments also indicate that the PSiC with pH value of 1.5 exhibits better coagulation performance in removing turbidity, COD and chroma of paper mill wastewater.

1. Introduction

Inorganic polymer coagulants are widely used in wastewater treatment for effective removal of suspended solids and natural organic matters [1–4]. Polysilicate complex coagulants are a type of inorganic polymer coagulant developed for decades on the basis of poly-silicic acid (PS) and metal salts. Preparation and characterization of polysilicate complex coagulants are studied extensively as they have distinct abilities of charge neutralization, adsorption bridging and sweep coagulation in removing colloidal particles [5]. Composite-polymerization and co-polymerization are two conventional methods to prepare polysilicate complex coagulants. The former is polymerization of PS and hydroxylated metal salts, and the latter is hydroxylation of mixture of metal salts and PS [6,7]. These coagulants are often prepared from expensive industrial-grade materials. In recent years, few studies have been carried out to improve the coagulation efficiency or reduce the costs by developing novel coagulants from industrial wastes, such as galvanized aluminum slag, oil shale ash, fly ash and so on [8–10]. Currently, synchronous-polymerization was developed to synchronize the polymerization of silicate and the hydroxylation of metal salts [2,3].

Many factors will influence the characterization and coagulation performance of polysilicate complex coagulant, such as pH, silicon dose, aging time and aging temperature [11], especially pH. Polymerization of silicic acid is a complex process which involves formation of stable nuclei, growth of nuclei leading to fundamental particles and particle aggregation to form larger particles or other structures. The polymerization profile and attributes of the product are highly dependent on pH [12]. Furthermore, basicity is the ratio of the moles of added and/or bound bases to the moles of Al^{3+} or Fe^{3+} ions ($[OH^-]/[Al^{3+}]$ or $[OH^-]/[Fe^{3+}]$), and governs the nature of polymeric species and coagulation performance of polymerized Al/Fe (III) coagulants. Coagulation treatment of eutrophicated raw water showed that basicity of polyferric chloride influenced density, stability and color of flocs. Besides, hydrolysis of polyferric chloride with a higher basicity was slowed down in water and resulted in less residual iron [13]. Aluminum-silicate polymer composite (PASiC) coagulant with different basicity values from 1.2 to 2.0 were prepared, the coagulation efficiency

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of PASiC increases with the rising basicity, however, the PASiC products tend to become cloudy or partly gelatinous when basicity is too high, which will make them loss some coagulation efficiency [1]. pH is correlated with basicity to some extent, so it has important effect on speciation distribution of coagulant [14,15]. As pH can be easily measured, it is suitable for use as an industrial production control indicator. Nevertheless, there is little research on the effects of pH on the characterization and coagulation performance of polysilicate complex coagulants, and even less research on structure and morphology of polysilicate complex coagulants with different pH prepared by synchronous-polymerization.

In this paper, PSiC was prepared from fly ash, pyrite slag and wasted sulfuric acid by synchronous-polymerization, which simplifies the preparation process and reduces costs. The structures and morphologies of PSiCs at varying pH were characterized by X-ray diffraction (XRD), infrared spectra (IR), ultraviolet/visible absorption (UVA) scanning and microscopic imaging. Furthermore, their coagulation performances were evaluated by jar test in papermaking wastewater treatment.

2. Materials and methods

2.1. Materials

The studied industrial wastes include fly ash, pyrite slag and wasted sulfuric acid, which were obtained from Meixian Sulfuric Acid Plant, Baqiao Thermal Power Plant, and Xi'an Modern Chemistry Research Institute (China), respectively. The compositions of the industrial wastes are shown in Table 1.

Papermaking wastewater was used to verify the coagulation performance of PSiC. The wastewater is a yellow fluid with COD of 150 mg/L, turbidity of 66 NTU, chroma of 16 and pH of 7.5.

2.2. Preparation of PSiC

Preparation of PSiC could be divided into the following steps.

(a) Alkali leaching
About 50 g of fly ash and 165 mL of 6 mol/L sodium hydroxide (industrial grade) were added into a beaker and were stirred and heated to 80–90 °C for 2 h. After that, the leaching liquid was filtered. The solution contains 0.4 mol/L SiO_2. The insoluble ash particles and 100 mL of water were added into the beaker under stirring and dried.

(b) Acid leaching
Then 45 g of pyrite slag, 10 g of alkali-leached fly ash and 147 mL of 6 mol/L wasted sulfuric acid were added into the beaker under stirring, and heated to 80–90 °C for 2 h. Finally the mixture was filtered. The supernatant part contains 1.2 mol/L Fe^{3+}, 0.12 mol/L Al^{3+} and little other metals.

Table 1
Composition of industrial wastes.

Composition	Concentration of fly ash (wt.%)	Concentration of pyrite residual (wt.%)	Composition of waste sulfuric acid (wt.%)
Al_2O_3	27.67	4.78	–
Fe_2O_3	9.56	50.43	–
SiO_2	56.78	22.27	–
CaO	1.57	2.58	–
MgO	1.25	0.63	–
K_2O	1.12	1.57	–
SO_3	0.55	7.2	–
Na_2O	0.4	0.82	–
ZnO	0.5	1.83	–
Other	0.6	7.89	18.23
Nitric acid	–	–	9.41
Sulfuric acid	–	–	69.26
Nitrogen tetroxide	–	–	3.20

(c) Polymerizing
About 50 mL of the solution in step (a) was added at 1.5 mL/min into 19 mL of the solution in step (b), and then waste sulfuric acid was used to adjust pH. The solutions were aged at normal temperature for 2 days and PSiC was made.

2.3. Characteristics of PSiC

The liquid coagulants were dried at 50 °C for 20 h and ground into powders, which were analyzed with a D/MAX-RB X-ray diffractometer (Rigaku, Japan). Then the solid samples were measured by a KBr pressed disc with a Tensor37 IR spectrophotometer (Bruker, Germany) and the spectra were recorded in the range of 4000–400 cm^{-1}. The coagulant solution was diluted by 400 times and scanned from 190 to 700 nm with a TU-1810 spectrophotometer (Puxi, China). The solution samples were dripped on glass slides and dried at normal temperature, and then were observed and photographed by a microscopic imaging system, which includes an XSP(2XC) electron microscopy, a complementary metal-oxide-semiconductor and a computer (the Fifth Factory of Optical Instruments, China).

2.4. Coagulation performance

Coagulation performance was evaluated by jar test using a ZR4-6 six-unit stirred system (Zhongrun, China). The coagulant was added into the wastewater sample, which was stirred rapidly at 150 r/min for 2 min, followed by slow stir at 30 r/min for 10 min and precipitation for 30 min. Finally, the supernatant was taken from 3 cm below the surface of test wastewater. Turbidity, COD and chroma were measured by an HI93703 (HANNA, Italy) turbidimeter, back titration (GB11984-89, China), and colorimetric dilution (GB11903-89, China), respectively.

The optimal dosage of the PSiC and optimal pH for coagulation are determined by pre-experiments, which are 80 mg/L and 7–8.5, respectively. Coagulation tests were repeated three times and the data were the result of average values.

3. Results and discussion

3.1. XRD analysis

Fig. 1 presents the XRD spectra and primary compounds of PSiC samples at varying pH. Every spectrum shows obvious diffractive peaks. From Fig. 1, we can see that PSiC mainly consists of $Al_2Si_{50}O_{103}$, but the spectra of diffractive crystals such as $Fe_2(SO_4)_3$, Fe_2O_3, Fe_3O_4, $Al_2(SO_4)_3$, Al_2O_3 and SiO_2 cannot be observed in PSiC. It indicates that Fe, Al, and Si were polymerized to some new compounds rather than remaining a simple mixture of the raw materials. Besides, the XRD spectra of PSiC samples at varying pH are not similar, which implies the effects of pH on the complexation degree and form of PSiCs. Except $Al_2Si_{50}O_{103}$, PSiCs with pH of 1.5 also contains $Na_3H(SO_4)_2$, $Fe_5Al_4Si_6O_{22}(OH)_2$, $Fe_4Al_4Si_2O_{10}(OH)_8$ and $Fe_7Si_8O_{22}(OH)_2$. However, the species of crystal compounds are reduced when pH is too low or too high. There are $Na_3H(SO_4)_2$, $Al_2Si_{50}O_{103}$, and AlOOH in PSiCs with pH of 1.2. When pH is 5, PSiC only consists of Na_2SO_4. It indicates that polymerization of Fe, Al and Si is more complex in PSiC with pH of 1.5 than other pH.

3.2. Analysis of IR spectra

The IR spectra of PSiCs at varying pH are shown in Fig. 2a–e, respectively. All spectra exhibit two peaks at 3500–3300 and around 1640 cm^{-1}, which are assigned to the stretching vibration of –OH and the bending vibration of the absorbed, polymerized and crystallized water in the coagulant, respectively [16,17]. The peak at 1405–1406 cm^{-1} could be attributed to the vibration of –OH [18], which corresponds to the same peak at 1401–1402 cm^{-1} in PSiCs with pH values of 1.2, 1.5 and 1.8. The intensities of the above peaks